Title

JULY MONTHLY PROGRESS REPORT: DISTRIBUTION OF As, Cd, Hg, Pb, Sb, AND Se DURING SIMULATED IN-SITU OIL SHALE RETORTING

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Publication Date

1980-08-01

UC-91
LBID-260

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August 28, 1980

TO: Bob Thurnau and Pat Fair

FROM: D. C. Girvin and A. T. Hodgson

RE: July Monthly Progress Report
Distribution of As, Cd, Hg, Pb, Sb, and Se
During Simulated In-Situ Oil Shale Retorting
LBID-260

TASK 1. ANALYTICAL METHODS FOR OIL AND WATER

The difficulties encountered with the analysis of shale oils for Hg have been partially resolved. The major problem has been the rapid loss of Hg, indicated by sharply decreasing ZAA sensitivity, with successive injections of shale oil samples into the 1000°C WO_3 combustion tube. It was suspected that sulfuric and nitric acids were forming and accumulating in the exit of the combustion tube during combustion of the oil. The acids could then scrub the Hg from the carrier gas before it reached the Au amalgamation tube. To prevent this loss, the exit of the combustion tube was shortened, and the lead acetate bubbler and ascarite column were removed and replaced with a small bubbler containing 1.5% HCl. After combustion of each sample, sodium borohydride is injected into the acid bubbler to evolve the trapped Hg for collection on an amalgamation tube. Mercury collected on this tube is then thermally desorbed and swept into the ZAA in a stream of helium carrier gas. These modifications resulted in a substantial improvement in results for shale oils. However, there is still some loss in ZAA sensitivity with successive oil samples. This persistent problem may be due to a decrease in the oxidizing capacity of the WO_3 packing.

Five shale oil samples have been submitted for neutron activation analysis (NAA). The samples were sealed in quartz ampules and irradiated at the University of California reactor at Berkeley. They are now cooling down prior to gamma counting for Hg. The NAA results will be used to

evaluate the WO_3 combustion-amalgamation-ZAA method described above.

TASK 2. ANALYTICAL METHODS FOR GAS SAMPLES

As noted in the June 1980 monthly progress report, the weights of Hg in the offgas of retort runs LBL-02 and LBL-03 accounted for 39% and 43%, respectively, of the Hg initially present in the raw shale. These values are low in comparison with values discussed in a review of earlier mass balance studies (Fox, 1980). To determine if our ZAA measurements of Hg in offgas are accurate, two independent checks of the ZAA method will be conducted during the next retort run in August. Proposed methods and preparations for these tests are described below.

First, Au amalgamation tubes will be used to collect Hg in the offgas stream. These samples will be subsequently analyzed using a method similar to that described for oils. These discrete, independent measurements of Hg concentrations during the retort run can then be compared with the continuous ZAA results. This comparison will provide some insight into the relative accuracy of the two methods. However, even if both methods agree, the question of the possibility of a fraction of the Hg in the offgas stream escaping detection still remains.

The second test addresses this question. A high temperature (2000^{o}C), graphite combustion tube furnace will be installed upstream of the stainless steel ZAA furnace which normally operates at 900^{o}C. This high temperature combustion tube furnace will be turned on periodically during the retort run. If the response of the ZAA increases, this would indicate that there are forms of Hg in the offgas that are not thermally decomposed to elemental Hg at 900^{o}C and, therefore, are not normally detected by the ZAA. Incomplete decomposition could, in part, explain the relatively low percentage of Hg that occurs in the offgas.

A Perkin Elmer HGA 2000 heated graphite furnace is being used for the above test. It is currently being modified so that a continuous stream of offgas can be heated to approximately 2000^{o}C for 10 minute intervals. The necessary modifications include the fabrication of a baffled graphite tube to improve thermal contact of sample gas with the 2000^{o}C surfaces of the tube and the fabrication of cooled flanges to connect the offgas stream tubing to the furnace assembly. When these are completed, the entire unit must undergo

operational and leak tests.

Ancillary Activities

Two group members attended a three day, Colorado School of Mines, training program entitled "Shale Oil: Its Production, Properties, and Utilization". This program was conducted in Laramie, Wyoming on July 28-30.

PROJECTED WORK

The projected work for August is as follows:

Task 1. Analytical Methods for Oil and Water

- Evaluation of the method for Hg analysis in oil, described in this report, will continue.

Task 2. Analytical Methods for Gas Samples

- Modifications and testing of the high temperature graphite combustion tube furnace will be completed so the furnace can be used with the ZAA Hg monitor during the August retort run.

Task 4. Laboratory Partitioning Studies

- An inert gas retort run with continuous on-line Hg monitoring and several additional Hg experiments is scheduled for August.

Task 5. Field Studies

- Several group members will visit lease tract C-a, lease tract C-b, Logan Wash, Colony Development Co., and Geokinetics in August. Inspection of the facilities may be useful in siting the Hg field experiments to be conducted later in the study.

REFERENCE

J. P. Fox, "The Partitioning of Major, Minor, and Trace Elements During Simulated In-Situ Oil Shale Retorting," Ph.D. Dissertation, University of California, Berkeley, CA 1980 (LBL-9062)

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